

Lead dioxide coated hollow glass microspheres as conductive additives for lead acid batteries

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The major reason for the inability of a lead acid battery to achieve higher specific free energy values is that much of the active material in both the positive and the negative electrode is not discharged. Using conductive additives, such as lead dioxide-coated hollow glass microspheres, in the electrodes would improve the utilization of active material and could significantly increase the specific energy of the lead acid batteries. In this paper, we present a method for making hollow glass microspheres conductive by coating them with lead dioxide via the electroless deposition technique.

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Lead acid batteries have long been used in gasoline-driven cars primarily to provide the high current required by starter motors. The lead acid battery also has a high volumetric energy density, high specific power performance and high power density. These features, coupled with the low cost of materials, makes the lead acid battery an excellent power source for use in electric and hybrid electric vehicles. Improving the specific energy performance would help both types of vehicle to achieve a longer electric driving range. The theoretical specific energy of the lead acid battery is 176 Wh Kg^{-1} . The specific energy achieved in reality depends on the discharge rate, and is typically 15–25% of the theoretical value. Although the overall chemical reaction that runs the lead acid battery is well known, some of the mechanisms that limit the reaction under different conditions are not well understood. During charging, the positive plate paste contains lead dioxide, which is the positive active material. The negative plate contains a negative active material, such as sponge lead. During discharging of the lead acid battery, the lead dioxide in the positive plate and the lead in the negative plate are converted to lead sulfate. The lead sulfate is an insulator, which cre-

ates a non-conducting coating on lead dioxide. This decreases the active utilization of the battery. Therefore, the major reason for the inability of a lead acid battery to attain its theoretical specific energy is that much of the active material in both the positive and the negative electrode is not discharged.

In an attempt to better understand lead acid batteries and the physical processes that limit capacity, computer models have been developed that simulate the conductivity of the positive active material and the diffusion of sulfate ions [1–4]. It has been found that after a certain amount of the active material has reacted the remaining material becomes isolated and cannot react. The amount of active material that can be discharged before the remaining material becomes isolated is termed the critical volume fraction. Values for the critical volume fraction have been estimated to be approximately 60–70% for homogeneous paste. A model has been developed that estimates the critical volume fraction of paste containing non-conducting or conducting additives.

To model the conductivity of the active material, the material is assumed to be made of spherical particles and these are modeled as nodes on a two-dimensional grid. In the model, the active material is represented as a square node and the smallest additive shown in Figure 1 (i.e. 1×1) is one node. The 2×2 additive would

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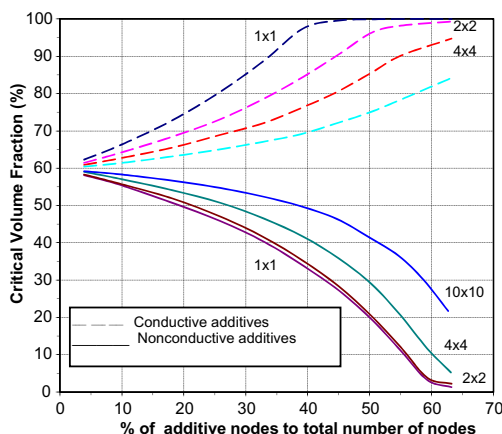


Figure 1. Utilization curves for active material with additives.

therefore represent four nodes in the model. From our observations, a 1×1 particle in the model corresponds to an approximately $5 \mu\text{m}$ (i.e. $1\text{--}10 \mu\text{m}$) particle in the active material. Each node is connected to the surrounding eight nodes by a conductive pathway. The grid contains over one million (1024×1024) nodes. The model randomly chooses a node and attempts to find a conductive pathway to the edge of the grid. If a pathway can be found, the starting node is considered discharged. If a pathway is not found, the starting node is marked as isolated. After all nodes have been selected and pathways have been tried, the model reports the number of nodes that were either discharged or isolated. The critical volume fraction is calculated as the ratio of discharged nodes to the initial number of available nodes. The critical volume fraction is the highest utilization that can be achieved when the reaction is not limited by diffusion. For a given volume percentage of additives, the large particles concentrate the nodes so that the additives are not as dispersed as the smaller particles. This causes the larger conductive particles to be less effective than the smaller particles for improving the critical volume fraction or active material utilization. Conversely, the larger non-conductive additives are not as detrimental as the smaller particles to the utilization of the active material. The strategy, therefore, would be to use small, conductive additives to improve utilization and large non-conductive particles for structure and filler, so that the reduction in utilization is minimized.

Figure 1 shows the critical volume fraction of paste having different additives plotted against the percent of additive volume. In Figure 1 the different curves represent different size additives, with the higher critical volume fraction curves associated with conductive additives and the lower curves with non-conductive additives. From Figure 1 it can be inferred that the utilization can be improved with small, conductive additives, whereas large non-conductive additives do not significantly reduce utilization until a large percentage is used. Note that when no additives are used, the critical volume fraction is about 60%.

Based on the findings of our model, our goal was to develop paste additives to increase both the power and energy densities of the lead acid battery. Specifically,

we were interested in developing hollow glass microspheres (HGMs) with a conductive layer to improve paste conductivity. Also, taking into consideration the acid-resistant and electrically conducting nature of lead dioxide, coupled with the ease and spontaneity associated with the electroless deposition technique, the present study was undertaken with the objective of developing HGMs coated with conductive lead dioxide using the electroless deposition technique.

The raw materials used for the present study included commercially available HGMs, lead acetate, ammonium acetate and potassium persulfate. The bath for electroless deposition was prepared by heating lead acetate solution, to which ammonium acetate and potassium persulfate solution were added. The pH of the electroless deposition bath was maintained using ammonia solution. The HGMs to be coated were placed in the bath and the temperature of the bath was raised to 80°C . Deposition was carried out for 20 min.

To measure the specific resistance of PbO_2 , PbO_2 film was deposited on a glass slide using the same conditions as used to coat the HGMs. The specific resistance was measured using the two-probe method. The PbO_2 film deposited on the glass slide was also studied by X-ray diffraction (XRD) using a Philips X-ray diffractometer with $\text{Cu } K_\alpha$ radiation. PbO_2 -coated HGMs were studied for their surface morphology under an Amray 1830 scanning electron microscope.

Electroless plating, also known as chemical or autocatalytic plating, is a non-galvanic plating method that involves several simultaneous reactions in an aqueous solution, which occur without the use of external electrical power. The reaction is accomplished when hydrogen is released by a reducing agent (normally sodium hypophosphite) and oxidized, thus producing a negative charge on the surface of the part. Electroless deposition is more widely used to deposit metals such as nickel and copper. To facilitate electroless deposition, the substrate is subjected to pretreatment processes consisting of pre-cleaning, sensitization and activation prior to actual deposition.

Anodic oxidation of some metal ions in aqueous solutions leads to deposition of an oxide at the anode [5,6]. Using this method, it is possible to deposit thin films of high-conductivity transparent oxides, such as PbO_2 , MnO_2 and Ti_2O_3 , from their corresponding ionic solutions. These oxides can also be deposited via electroless deposition by a heterogeneous reaction using an oxidizing agent instead of an external electrical current. Electroless deposition of oxides is possible in cases where the resulting oxide is electrically conductive. The reactions involved can be represented as follows:

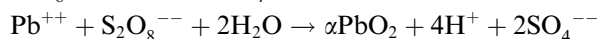
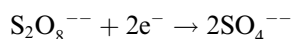
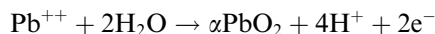


Figure 2 is a scanning electron micrograph of HGMs coated with PbO_2 using the electroless deposition technique. Most of the HGMs were uniformly coated, though a few HGMs showed a small discontinuity in the coated surface, as indicated by the arrow in Figure 2. Another prominent feature in Figure 2 is the large

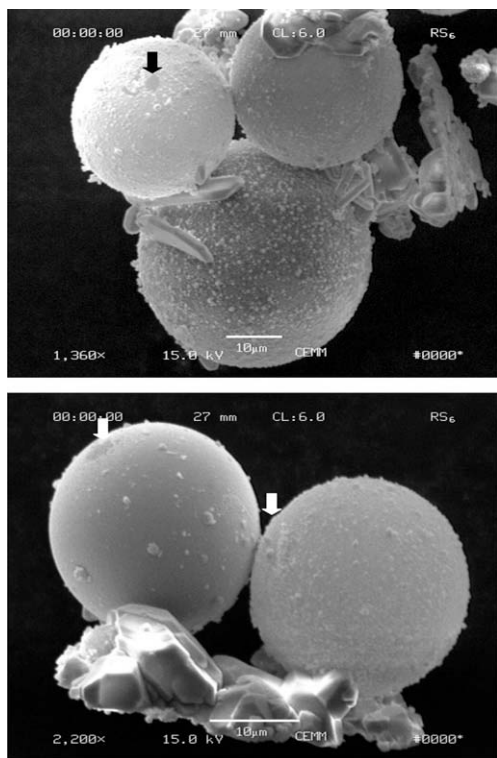


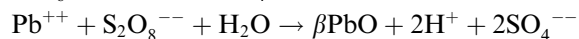
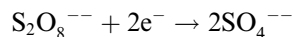
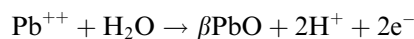
Figure 2. Scanning electron micrographs of HGMs coated with PbO₂ using the electroless deposition technique.

PbO₂ crystals that grow alongside the PbO₂-coated HGMs. These PbO₂ crystals are very large in comparison to the PbO₂ crystals on the HGM surface. This difference in size and morphology can be explained on the basis of the nucleation process. During electroless deposition, the HGM surface promotes heterogeneous nucleation. Because the PbO₂ nuclei formed on the HGM surface are large in number, they are small in size. The

big, well-defined PbO₂ crystals that grow alongside the coated HGMs are probably formed via homogeneous nucleation.

The X-ray pattern of PbO₂ deposited on a glass slide via electroless deposition revealed the presence of two predominant phases, namely alpha PbO₂, which has an orthorhombic structure (scrutinyite), and beta PbO (massicot), which also has an orthorhombic structure (Fig. 3). The presence of the scrutinyite phase imparts a characteristic dark brown appearance to the PbO₂ deposited on the glass slide. Compared to the XRD peaks of alpha PbO₂, the peaks of beta PbO are very sharp. This means that the alpha PbO₂ phase formed during electroless deposition is less crystalline compared to the beta PbO phase. Shortening of the PbO₂ peaks also means that the PbO₂ phase formed during the electroless deposition process is non-stoichiometric, with a strained or distorted lattice structure. The strong PbO peaks in the XRD pattern shown in Figure 3 also suggests that the amount of PbO formed is sizable compared to the amount of PbO₂. PbO is electrically non-conducting; therefore any attempt to suppress PbO formation during the electroless deposition process is likely to enhance the electrical conductivity of the coated material.

PbO is formed by the partial oxidation of lead ions as per the following reaction:



The transformation between PbO₂ and PbO is reversible in nature and the equilibrium can be shifted in either direction by irradiation with an electron beam. In the present case, the variation in pH during the electroless deposition is probably what caused the partial oxidation that led to the formation of both PbO and PbO₂.

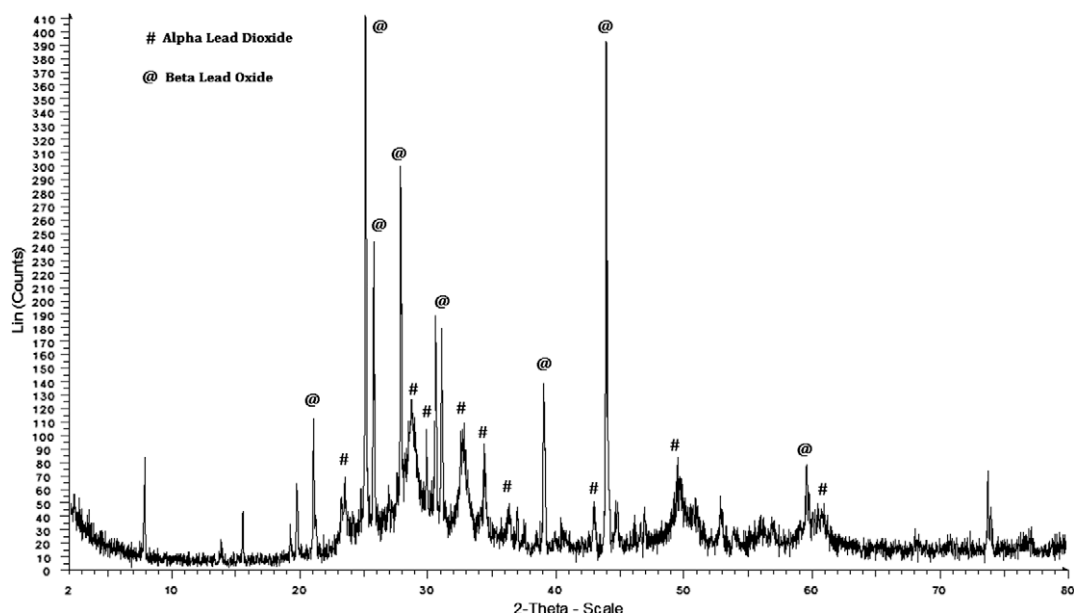


Figure 3. X-ray diffraction (XRD) pattern of the glass slide coated with PbO₂ using the electroless deposition technique.

Using the current v/s voltage curve generated using the two-probe method, the specific resistance computed for the PbO_2 film using electroless deposition conditions identical to those used to coat HGMs was found to be $3.5 \times 10^{-6} \Omega\text{m}$. The specific resistance of the PbO_2 film deposited on the glass slide is fairly high compared to that of silver, which has a specific resistance of $1.5 \times 10^{-8} \Omega\text{m}$, but is comparable to specific resistance of manganese, with a specific resistance value of $1.35 \times 10^{-6} \Omega\text{m}$, and way below the specific resistance of most the inorganic oxides. The conductivity of the PbO_2 deposited via electroless deposition can be further enhanced by suppressing the formation of the non-conducting PbO phase during the deposition process.

In summary, HGMs were successfully coated with a conductive layer of PbO_2 via the electroless deposition technique. The conductive HGMs so developed could

be used as conductive additives to improve the specific energy of the lead acid battery. The findings of the present study can be used to improve the performance of lead acid batteries. This could pave way for the use of lead acid batteries in plug-in hybrid electric vehicles.

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